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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the electrode active material of the nonaqueous electrolyte battery of a rechargeable battery.

[0002]

[Description of the Prior Art]In recent years, the demand of portable devices, such as a cellular phone, a laptop PC, and a camcorder/movie, is increasing. A small lightweight rechargeable battery is indispensable to these apparatus. Although the nickel-Cd cell and the Ni-H battery are mainly used as a rechargeable battery now, these cells are coming to the limit of the small weight saving.

[0003]On the other hand, development of the nonaqueous electrolyte secondary battery which uses occlusion and the substance from which it can be desorbed is advanced to the negative electrode in metal lithium and lithium. High tension is obtained compared with an old small rechargeable battery, and also this cell has the feature that an energy density is high, and can build a lightweight rechargeable battery smaller than an old cell.

[0004]Although LiCoO_2 is generally used for the electrode of this cell, Since there are problems, like the price of Co is high and there are few deposits, compared with LiCoO_2 , it is cheap, lithium nickel multiple oxides, such as LiNiO_2 from which high charge and discharge capacity is moreover obtained, attract attention as a new electrode active material, and research is advanced.

[0005]By J.Am.Chem.Soc.76-1499 (1954), USP No. 4,302,518, etc., the synthetic method of a lithium nickel multiple oxide is publicly known, generally mixes a lithium compound and a nickel compound, and is acquired by calcinating at 500-900 °C according to oxygen environment.

[0006]It is clear that the battery capacity of $\text{LiNi}_{1-t}\text{N}_t\text{O}_2$ (N is Li, nickel, elements other than O,

and $0 < t \leq 0.5$) which replaced some nickel of LiNiO_2 by other elements is excellent in these days. For example, in the example of JP,6-215800,A, aluminum, Ga, B, Sc, Fe, Cr, Mn, Ti, etc. are used as N, and it is described that the charge and discharge energy and the conservation characteristic of the cell using this electrode active material are excellent.

[0007]

[Problem(s) to be Solved by the Invention]Although LiNiO_2 is a material excellent in the field of a price and charge-and-discharge capacity, there is a problem that preservation stability, especially the stability to moisture are missing compared with LiCoO_2 . When using LiNiO_2 as fines and using it as an electrode active material, especially since specific surface area becomes large, it is easy to be influenced by moisture. For example, when a cell is constructed using LiNiO_2 placed into the air with large humidity after grinding, When initial service capacity falls or charge and discharge are repeated, there is a problem that service capacity falls remarkably, and the important question of safe -- occasionally generation of heat occurs inside a cell -- might arise.

[0008]

[Means for Solving the Problem]In order to solve an aforementioned problem of this invention, as a result of inquiring wholeheartedly, it is general formula $\text{Li}_x\text{Ni}_y\text{N}_z\text{O}_2$ (N). [Li and] It is a lithium transition metal M multiple oxide (M is one or more sorts of Co, Mn, and Fe, and) about the surface of nickel, elements other than O, $0.8 < x < 1.2$, $0.8 < y + z < 1.2$, and a lithium nickel multiple oxide shown by $0 \leq z < 0.2$. a thing containing some nickel -- containing -- it solved by coating.

[0009]That is, this invention is ** general formula $\text{Li}_x\text{Ni}_y\text{N}_z\text{O}_2$ (N). [Li and] It is a lithium transition metal M multiple oxide (M is one or more sorts of Co, Mn, and Fe, and) about the surface of nickel, elements other than O, $0.8 < x < 1.2$, $0.8 < y + z < 1.2$, and a lithium nickel multiple oxide shown by $0 \leq z < 0.2$. a thing containing some nickel -- containing -- an electrode active material of a coating nonaqueous electrolyte battery, and the ** transition metal M (M is one or more sorts of Co, Mn, and Fe, and) A compound and a lithium compound containing a thing containing some nickel are dissolved or suspended to a solvent, general formula $\text{Li}_x\text{Ni}_y\text{N}_z\text{O}_2$ (N -- Li and nickel.) Elements other than O, $0.8 < x < 1.2$, $0.8 < y + z < 1.2$, and a lithium nickel multiple oxide shown by $0 \leq z < 0.2$ are added, and it is considered as a slurry, and is related with a manufacturing method of an electrode active material of a nonaqueous electrolyte battery drying and calcinating this slurry.

[0010]

[Embodiment of the Invention]Although the lithium nickel multiple oxide shown by general formula $\text{Li}_x\text{Ni}_y\text{N}_z\text{O}_2$ (N is Li, nickel, elements other than O, $0.8 < x < 1.2$, $0.8 < y + z < 1.2$, and

0<=z<0.2) was obtained with the publicly known synthetic method and is enough, When it is included in a cell as an electrode active material, without putting it to a watery atmosphere, it is necessary to fully act as an electrode active material. The contained element N in particular is not limited.

[0011]As a lithium nickel multiple oxide used for this invention, LiNiO_2 , $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$, $\text{LiNi}_{0.9}\text{Al}_{0.1}\text{O}_2$, $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$, etc. are mentioned, for example.

Although what kind of shape may be sufficient as shape of this, the thing near especially a globular form is preferred.

[0012]As for the lithium transition metal M multiple oxide formed in the surface, it is preferred that it is what acts as an electrode active material in itself. As an example, a lithium cobalt multiple oxide, a lithium manganese multiple oxide, the lithium cobalt multiple oxide containing some nickel, etc. are mentioned. As for the compound and lithium compound of the transition metal M, a nitrate, carbonate, acetate, hydroxide, an oxide, a peroxide, metal, etc. are mentioned. As for these, it is preferred that it is what is dissolved or suspended to the solvent used. As a solvent used for the compound and lithium compound of the transition metal M, what can be used for lithium ion battery organic electrolysis liquid, such as organic solvents, such as water or alcohol, and benzene, or propylene carbonate, can be used.

[0013]Although it is suitably chosen by the boiling point of a solvent, etc., when water is used, for example, in order to make removal of moisture perfect, the temperature of not less than 90 °C is preferred [drying temperature]. Although a drying method in particular is not limited, since the compound by which surface coating is carried out will be uniformly distributed on lithium nickel multiple oxide particles if spray drying processes, such as a spray dryer, are used, it is preferred.

[0014]As for calcination temperature, it is preferred that it is calcination temperature suitable for a coating substance being compounded as an electrode active material, and is the calcination temperature to which basic structure of a lithium nickel multiple oxide is not changed, and it is suitably chosen according to the balance of both quantity. As for a firing environments, it is preferred that it is the oxygen existence atmosphere which promotes oxidation, and calcinating further, removing decomposition production gas is preferred.

[0015]As for the mean particle diameter of an electrode active material, since the thickness of the electrode made by applying an electrode active material to a charge collector needs to turn into a thickness of hundreds of microns or less, it is preferred to consider it as less than 50 microns. As for the mean particle diameter of an electrode active material, since application to a charge collector and mixing with a conducting material will become difficult if the mean particle diameter of an electrode active material is too small, it is preferred to exceed 1 micron.

[0016]Although survey of the thickness of the coating substance of the lithium nickel multiple oxide surface is difficult, it is preferred that the average thickness calculated from the mean

particle diameter of a lithium nickel multiple oxide, the addition of a coating substance, density, etc. shall be 0.001 microns or more 5 microns or less. . Since it becomes impossible to pull out battery capacity called the high capacity which is the feature of a lithium nickel multiple oxide when the thickness of coating exceeds 5 microns, it is not desirable. Since it becomes impossible for the thickness of coating to achieve the duty of coating in less than 0.001 micron and the purpose of this invention is not attained, it is not desirable. Although the compounded electrode active material has the stability to moisture, since the decomposition reaction of water, etc. will occur and the problem of safe will arise if moisture goes into the inside of a cell when producing a cell, it is preferred to perform cell production after desiccation of an electrode active material.

[0017]The method of manufacturing the above and the electrode active material of a nonaqueous electrolyte battery, The compound of the transition metal M (M contains what is one or more sorts of Co, Mn, and Fe, and contained some nickel), and the compound of lithium are dissolved or suspended in a solvent, The lithium nickel multiple oxide shown by general formula $\text{Li}_x\text{Ni}_y\text{N}_z\text{O}_2$ (N is Li, nickel, elements other than O, $0.8 < x < 1.2$, $0.8 < y < 1.2$, and $0 \leq z < 0.2$) is added, and it is considered as a slurry, and is obtained by the method of drying and calcinating this slurry.

[0018]Although it can manufacture also by the method of coating by mixing with the granular material of a direct lithium nickel compound, and calcinating the fines of a lithium transition metal M multiple oxide, Since a lithium transition metal M multiple oxide does not distribute uniformly on the surface of lithium nickel multiple oxide particles, and improvement in stability may not be found depending on the case, it is not desirable.

[0019]The electrode active material obtained by the above-mentioned method is excellent in preservation stability, and even if placed by the atmosphere containing moisture, if a cell is assembled after desiccation, it will not reduce the capacity of the assembled cell. Problems, such as generation of heat, are not produced and the thing excellent in safety is obtained. The electrode active material of the nonaqueous electrolyte battery of this invention may be used for any of an anode or a negative electrode.

[0020]

[Example]Hereafter, the example of this invention is given and it explains still in detail.

After carrying out weighing of 83.9 g of example 1 lithium-hydroxide monohydrate, and the nickel hydroxide 185.4g (atomic ratio Li/nickel(mole ratio) =1.0 of lithium and nickel), a ball mill may be used, and it ground and mixed, and dried at 150 °C for 12 hours. After calcinating this dry thing at 750 °C according to oxygen environment for 5 hours, the ball mill ground in a nitrogen atmosphere for 1 hour, and the lithium nickel multiple oxide with a mean particle diameter of 7 microns was obtained. Coating treatment was performed by the following methods. The lithium nitrate 3.4g and cobalt nitrate 6 hydrate 14.6g (Li/Co(mole ratio) =1.0) is

dissolved in 300 g of ethanol, the lithium nickel multiple oxide 92.7g (Co/nickel(mole ratio) =0.05) obtained above was added to this, and it was distributed. After the outlet temperature of the spray dryer dried these dispersion liquid on the conditions used as about 100 **, the electrode active material which coated with 700 ** by calcinating for 1 hour according to oxygen environment was obtained using the electric furnace. In order to investigate the stability of an electrode active material, the following processings and a battery capacity examination were done. First, after settling the obtained electrode active material on the atmosphere of the temperature of 60 **, and 90% of relative humidity for 1 hour, it dried at 120 ** for 1 hour. Next, the polyfluoroethylene which is acetylene black and the binding material which are an electrode active material and a conducting material was kneaded by the specified weight ratio, and it molded into the pellet type, and was considered as the electrode. To the negative electrode, the electrolysis solution assembled the button type battery using the propylene carbonate / diethyl carbonate mixed liquor which carried out 1 mol/L dissolution of the lithium hexafluorophosphate using metal lithium. In order to investigate the performance of this cell, charge and discharge were carried out by the constant current of 0.5 mA/cm² in the voltage range of 4.2-3.0V, and the service capacity after the first stage and 50 cycles was measured. A result is shown in Table 1.

[0021]After carrying out weighing of the example 2 lithium nitrate 137.9g and the nickel hydroxide 185.4g (the atomic ratio of lithium and nickel is Li/nickel(mole ratio) =1.0), a ball mill may be used, and it ground and mixed, and dried at 150 ** for 12 hours. After calcinating this dry thing at 700 ** according to oxygen environment for 10 hours, the ball mill ground in a nitrogen atmosphere for 1 hour, and the lithium nickel multiple oxide with a mean particle diameter of 12 microns was obtained. Coating treatment was performed by the following methods. 2.1 g of lithium hydroxide monohydrate and the cobalt nitrate 6 hydrate 14.6g (Li/Co (mole ratio) =1.0) are dissolved in 300 g of ethanol, the lithium nickel multiple oxide 92.7g (Co/nickel(mole ratio) =0.05) obtained above was added to this, and it was distributed. After the outlet temperature of the spray dryer dried these dispersion liquid on the conditions used as about 100 **, the electrode active material which coated with 700 ** by calcinating for 1 hour according to oxygen environment as well as Example 1 was obtained. In order to investigate the stability of this electrode active material, the same processing as Example 1 and a battery capacity examination were done. The result of service capacity is shown in Table 1.

[0022]The lithium nickel multiple oxide was obtained by the same method as Example 1 except having changed example 3 starting material into 83.9 g of lithium hydroxide monohydrate, the nickel hydroxide 166.9g, and 15.6 g (it is the mixture ratio Li/nickel/aluminum(mole ratio) =1.0/0.9/0.1) of aluminium hydroxide. In order to investigate the stability of the electrode active material obtained by coating with the same method as Example 1, the same processing as Example 1 and a battery capacity examination were done. The result of service capacity is

shown in Table 1.

[0023]The lithium nickel multiple oxide was obtained by the same method as Example 1 except having changed example 4 starting material into 83.9 g of lithium hydroxide monohydrate, the nickel hydroxide 166.9g, and the basic cobalt carbonate 137.0g (it is the mixture ratio Li/nickel/Co(mole ratio) =1.0/0.9/0.1). In order to investigate the stability of the electrode active material obtained by coating with the same method as Example 1, the same processing as Example 1 and a battery capacity examination were done. The result of service capacity is shown in Table 1.

[0024]The lithium nickel multiple oxide was obtained by the same method as example 5 Example 1. Coating was performed like Example 1 except having changed the solvent at the time of coating into water. In order to investigate the stability of this electrode active material, the same processing as Example 1 and a battery capacity examination were done. The result of service capacity is shown in Table 1.

[0025]The same processing as Example 1 and a battery capacity examination were done except not performing coating treatment using the lithium nickel multiple oxide obtained in comparative example 1 Example 1. The result of service capacity is shown in Table 1.

[0026]The same processing as Example 1 and a battery capacity examination were done except not performing coating treatment using the lithium nickel multiple oxide obtained in comparative example 2 Example 2. The result of service capacity is shown in Table 1.

[0027]The same processing as Example 1 and a battery capacity examination were done except not performing coating treatment using the lithium nickel multiple oxide obtained in comparative example 3 Example 3. The result of service capacity is shown in Table 1.

[0028]The same processing as Example 1 and a battery capacity examination were done except not performing coating treatment using the lithium nickel multiple oxide obtained in comparative example 4 Example 4. The result of service capacity is shown in Table 1.

[0029]

[Table 1]

	初期放電容量 (mA h / g)	充放電 50 サイクル後の 放電容量 (mA h / g)
実施例 1	1 6 8	1 5 2
実施例 2	1 7 1	1 5 2
実施例 3	1 6 0	1 4 9
実施例 4	1 5 8	1 5 0
実施例 5	1 5 5	1 4 2
比較例 1	1 4 2	1 2 1
比較例 2	1 3 8	1 2 1
比較例 3	1 1 5	1 0 6
比較例 4	1 3 3	1 1 7

The battery characteristic of the electrode active material after carrying out 1 time processing with 60 ** and 90% of relative humidity [0030]

[Effect of the Invention]The electrode active material of the nonaqueous electrolyte battery of this invention can increase the service capacity after the early stages of a cell, and 50 cycles by leaps and bounds by coating with a lithium transition metal M multiple oxide compared with the conventional lithium nickel multiple oxide. In conventional technology, the safe rechargeable battery excellent in the preservation stability which was not acquired and the stability to moisture can be obtained.

[Translation done.]